Field-Measured Oxidation Rates of Biologically Reduced Selenium in Sludge

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Sludge generated during surface-water transport or biological treatment of selenium laden agricultural drainage water contains high concentrations (20-100 mg/kg) of selenium. Finding safe and economical sludge disposal methods requires understanding of the biogeochemical processes that change selenium speciation (after placed at a disposal site.) Two experiments, each comparing 3 treatments for sludge disposal has resulted in data on changes in selenium speciation spanning an eight year period. Treatments included direct application to upland soils and application with tillage to depths of 15 cm and 30 cm. Soil cores, soil water samples and groundwater monitoring were used to track changes in selenium speciation and transport of re-oxidized forms of selenium. Measurements demonstrate the slow re-oxidation of reduced forms of selenium, largely elemental and organically associated forms, to selenate and selenite. Downward transport of these re-oxidized forms of selenium are driven by winter rains. Field measured re-oxidation rates for these field trials are presented and compared to selenium re-oxidation rates in formerly ponded areas at Kesterson Reservoir, California.

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Introduction

Sludge generated during surface-water transport or biological treatment of selenium-laden agricultural drainage water contains high concentrations (20-100 mg/kg) of selenium. These sludges contain reduced forms of selenium [Se(0) and organically associated forms] that are nearly insoluble under anoxic conditions. When these sludges are removed from their anoxic subaqueous depositional environment and placed in an oxidizing environment, re-oxidation of is expected to occur. Oxidized forms of selenium Se(IV) and Se(VI) are relatively soluble and mobile, and at high enough concentrations are toxic to wildlife and humans. Leaching and biological uptake of selenium reoxidized from these sludges may lead to unacceptable environmental impacts. Therefore, finding safe and economical sludge disposal methods requires an understanding of the rate of re-oxidation of selenium and subsequent transport into groundwater and biota.

Laboratory experiments have shown that reduced forms of selenium can be re-oxidized in oxic soils and bacterial cultures with rate constants on the order of 10^{-2} to 10^{-4} day^{-1} (Zawislanski and Zaverin, 1996; Dowdle and Oremland, 1998). Field-measured selenium re-oxidation rates in Kesterson Reservoir soils, California ,are at the low end of this range (Benson et al, 1992; Wahl and Benson, 1996).

Materials and Methods

The sludge used for this experiment was obtained from the San Luis Drain. It is dominated by mineral matter but contains from 1 to 5% organic carbon. Samples of sludge have been observed to accumulate over 100 mg/kg (dry-weight) of selenium. Speciation studies of these sludges using both synchrotron X-ray spectroscopic methods and sequential extraction techniques indicate that selenium is in reduced forms, primarily as Se(0) and organically associated Se. Reduced forms of selenium are believed to be concentrated in these sludges by a combination of dissimilatory bacterial reduction of selenium in the anoxic sludges and deposition of decaying biomass (e.g. algae and rooted aquatic vegetation). The relative contribution of each of these processes is unknown but it is likely that the contribution from decaying biomass is comparatively large.

Three treatments for sludge disposal were compared and experiments have resulted in data on changes in selenium concentrations and speciation spanning an 8-year period (1990-1998). The experiments were conducted at Kesterson Reservoir, California. Treatments included application to upland soils with tillage to depths of 30 cm (Test Plot 1), 15 cm (Test Plot 2), and direct application with no tillage (Test Plot 3). Sludge contained 59.3 ± 15.8 (n=5) mg/kg total selenium. The average water-

extractable concentration (5:1 water to soil extract) was 3.4 ± 2.5 (n=5) mg/kg, approximately 5% of the total selenium. Soil cores and groundwater monitoring were used to track changes in selenium speciation and transport of re-oxidized forms of selenium over an 8-year period.

Results and Discussion

Soil monitoring data comparing the concentration of selenium in 1990 to that measured in 1998 are shown in Figures 1 and 2 for total and water extractable selenium [Se(VI) & Se(IV)] from Test Plot 2. Similar data were obtained from the other test plots. No significant decreases in total selenium were observed over the 8-year period in any of the test plots. Significant decreases averaging 62% ($\pm10\%$ n=3) in the water extractable selenium concentration are observed in all test plots in the top 15 cm interval. Water extractable selenium concentrations increased (4 times) at 45 to 60 cm in in Test Plot 1 and decreased (0.5 times) in Test Plot 2 deeper in the profile (15 to 45 cm). No significant changes were observed in Test Plot 3. Water extractable selenium concentrations are dominated by Se(VI) (81% $\pm12\%$ n=12). No significant changes in the ratio Se(IV)/Se(VI) were observed over the 8-year period.

These data demonstrate that re-oxidation of selenium from these sludges is very slow and, most likely, lower than the lowest value reported in the above studies of 10^{-4} day^{-1}. Three lines of evidence support this conclusion. First, changes in total selenium concentrations in the treatment interval are not significant. While spatial variability will confound detection of small temporal changes, even with the observed spatial variability, declines associated with an oxidation rate of 10^{-4} day^{-1} should have been significant over the eight-year period (e.g., 25% decline would be expected). Second, water-extractable selenium concentrations declined in the treatment interval. If oxidation occurred at rates of greater than 10^{-4} day^{-1}, higher concentrations of Se(VI) and perhaps Se(IV) would be observed in the treatment interval (e.g., 5% of the total, rather than the 1 to 3% observed). Finally, large increases in the water extractable inventory of selenium would be expected deeper in the profile if oxidation rates were higher than 10^{-4} day^{-1}. Re-oxidation, followed by leaching due to winter rains (300 mm/year average) would be expected to lead to increases in water extractable selenium deeper in the profile, as observed by Tokunaga et al (1991).

Conclusions

The rates of selenium re-oxidation observed in this experiment are slow ($<10^{-4}$ day^{-1}) and appear to be slower than those measured in the laboratory and field studies cited above. Additional mechanistic studies that include the effect of depositional processes (assimilative vs. dissimilative reduction), presence and nature of soil organic matter, allotropes of Se(0) and mineral composition are needed to increase our understanding of the biogeochemical cycling of selenium.

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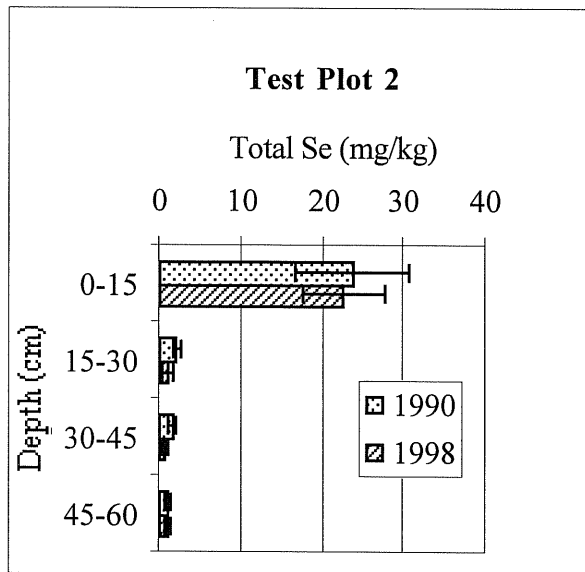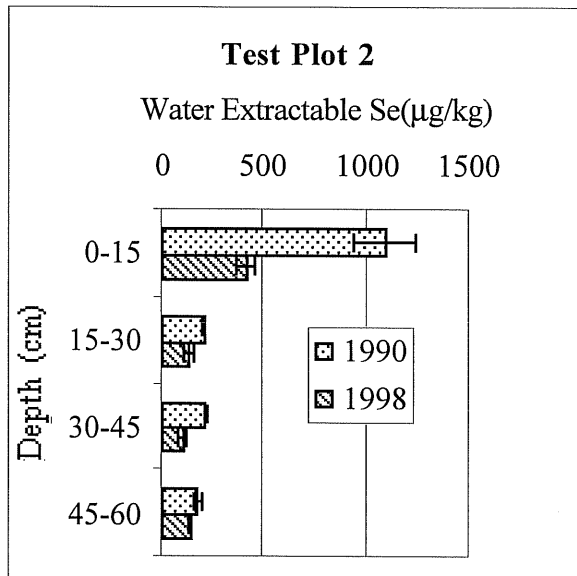
Figure 1. Total selenium (±1 std n=3).

Figure 2. Extractable selenium (±1 std n=3).